IPST Technical Paper Series Number 610

In-situ Measurement of Local Biodegradation During Secondary Treatment. Application to Bleached Pulp Mill Chloro-organics

C.L. Williams, S. Banerjee, T.E. Kemeny,
R. Sackellares, M.D. Juszynski, and M.E. Degyansky

March 1996

Submitted to
Environmental Science & Technology

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Chris L. Williams, Sujit Banerjee
Institute of Paper Science & Technology
500 Tenth Street N.W.
Atlanta, GA 30318

Thomas E. Kemeny, Robert Sackellares
Georgia-Pacific Corporation
PO Box 105605
Atlanta, GA 30348

Michael D. Juszynski
Georgia-Pacific Corporation
PO Box 1438
Brunswick, GA 31521

Milan E. Degyansky
Department of Engineering Technology
Georgia Southern University
Statesboro, GA 30460

Abstract

A procedure has been developed for mapping the biodegradation of effluent constituents in the water column of secondary treatment systems, and applied to chlorinated bleach plant components. Pulp is bleached with radioactive [^{36}Cl] Cl_2 or ClO_2 to give labeled AOX. Next, samples are drawn from various locations and depths in the treatment system, and the labeled AOX is added to each sample. The amended samples are transferred to vials capped at both ends with semi-permeable membranes. These restrict the microorganisms and most of the tagged AOX inside the vial, but allow flow of dissolved oxygen and nutrients. The vials are then inserted into a sampler at 1-ft intervals, which is then placed in the treatment system for a period equal to the hydraulic retention time of the lagoon. Thus, the radioactive AOX experiences the conditions prevalent in the lagoon while being held captive inside the vial. After retrieval of the sampler, the radioactivity remaining in each vial is determined, and the removal efficiency calculated.

Only 15% of the radioactive AOX biodegraded in the water column in the aerated stabilization basin (ASB) of the Georgia-Pacific facility at Brunswick, GA. This value was independently confirmed in a study where samples from the inlet and outfall of the treatment system were filtered through a 500 Da filter, and both the unfiltered and filtered samples were analyzed for AOX. Removal of the filtered AOX, which constitutes the potentially bio-

degradable fraction, was only 15% greater than that of the unfiltered material. Finally, the bulk of AOX reduction occurred very early in the treatment system.

Introduction

Bleaching pulp with chlorine or chlorine dioxide generates chlorinated residuals in the effluent. Chlorinated effluent components range from low molecular weight compounds such as chloroform to polymeric ionic species (1-6). Most of these constituents sorb to carbon, and they are collectively referred to as AOX, or adsorbable organic halides. Although roughly half of the influent AOX is removed during secondary treatment, the contribution of biodegradation relative to abiotic processes is unknown; removal under both aerobic (7,8) and anaerobic (9,10) conditions, settling (9,10), and chemical degradation (11) have all been suggested. Since the complexity of a treatment system cannot be fully replicated in laboratory work, we have studied the rate of AOX biodegradation in the field using two complementary techniques. The first involves a novel approach where the degradation of radiolabeled substrates is studied at a particular xyz coordinate in the lagoon. In the second, the degradation of a low molecular weight AOX subset is compared to that of the whole sample as it traverses the treatment system.

Approach

In-situ biodegradation

AOX biodegradation was studied in the field under controlled conditions by using a variation of a membrane sampler developed for a groundwater application (12). Radioactive AOX was first prepared by bleaching pulp with radioactive [^{36}Cl] Cl_2 or ClO_2. Next, samples were drawn from various locations and depths in the lagoon, and the labeled AOX was added to each sample. The samples were then transferred to vials capped at both ends with semi-permeable membranes, which hold the microorganisms inside the vials, but allow flow of dissolved oxygen and nutrients. The AOX diffuses out of the vials but at a rate slow enough for measurable biodegradation to occur inside. In this context, biodegradation refers to dehalogenation and not necessarily to mineralization. The vials were then inserted at 1-ft intervals into a sampler, which was placed in the treatment system for a period equal to the retention time in the treatment system. After retrieval of the sampler, the concentration of the labeled AOX was determined in each vial, and the removal efficiency calculated. Thus, the radioactive AOX experienced the conditions prevalent at a given x,y,z coordinate in the lagoon. A unique feature of our approach is that the radioactive AOX added can be distinguished from the AOX already present in the lagoon. The high precision and sensitivity associated with radioactivity measurements allows a controlled experiment to be conducted in the field.

The membrane holds the microorganisms captive in the vial, but permits partial leakage of the AOX. Ideally, we would prefer all the AOX to be contained in the vial, but a membrane of pore size small enough to achieve this also restricts flow of inorganic ions. Thus, we compromised on a membrane that allowed flow of nutrients and dissolved oxygen (DO), but which only partially restricted the outflow of radioactive AOX. In order to account

for nonbiological losses through diffusion, sorption, and chemical degradation, vials at alternate depth intervals were sterilized by adding formalin to its contents. Now, the difference in AOX concentrations between adjacent vials was taken to reflect biodegradation in the water column.

A complication is that AOX leakage is not necessarily uniform across the vials in a sampler, since, for example, the membrane surface in a given vial may be partially clogged by particulates in the lagoon. This was compensated for by using the $^{36}Cl^-$ already present in the solution as a product of bleaching as a conservative tracer. Since $^{36}Cl^-$ should only be lost through diffusion, the rate of $^{36}Cl^-$ removal can be used to normalize the rate of AOX diffusion. Since the diffusion of both AOX and $^{36}Cl^-$ was shown to follow first-order kinetics, the AOX lost through biodegradation could be obtained as follows.

The ratio of first-order rate constants for diffusional loss of AOX (k_{AOX}), and $^{36}Cl^-$ ($k_{chloride}$) from a sterilized vial is

$$\frac{k_{AOX}}{k_{chloride}} = \frac{\ln[AOX]_o - \ln[AOX]}{\ln[chloride]_o - \ln[chloride]} \quad (1)$$

This ratio is averaged for a pair of sterile vials straddling a "live" vial to give $(k_{AOX}/k_{chloride})_{sterile}$. The rate constant for diffusional AOX loss from a live vial is

$$(k_{AOX})_{diff} = (k_{AOX}/k_{chloride})_{sterile}\,(k_{chloride})_{live} \quad (2)$$

where $(k_{chloride})_{live}$ represents loss of chloride from the live vial. If $k_{AOX}/k_{chloride}$ for diffusional loss remains constant for both live and sterilized vials, then the above equation normalizes small differences in AOX diffusivity caused by variability in membrane permeability. AOX loss from the live vial due to diffusion can be expressed as

$$[AOX]_{diff} = [AOX]_o \exp(-k_{AOX})_{diff} t \quad (3)$$

$$= [AOX]_o \exp-(k_{AOX}/k_{chloride})_{sterile}\,(k_{chloride})_{live}\, t \quad (4)$$

$$= [AOX]_o \exp-(k_{AOX}/k_{chloride})_{sterile}\, \ln[chloride]_o/[chloride]_{live} \quad (5)$$

Hence, the amount of AOX biodegraded is

$$[AOX]_{bio} = [AOX]_{diff} - [AOX] \quad (6)$$

where [AOX] is the concentration remaining in the unsterilized vial.

In summary, the approach comprises the following steps.

1. Samples are drawn from various depths at a given location in the lagoon. Each sample is amended with a [^{36}Cl] AOX solution prepared from either $^{36}Cl_2$ or $^{36}ClO_2$ bleaching.

2. The amended samples are placed in vials capped on both ends with semi-permeable membranes. The membranes permit flow of oxygen and nutrients, hold the organisms in place, and partially restrict outflow of AOX.

3. The vials are placed in samplers at 1-ft intervals extending to the bottom of the lagoon. Vials at alternate depth intervals are sterilized. The vials are retrieved after a period equal to the hydraulic retention time of the lagoon.

4. The [^{36}Cl]AOX and $^{36}Cl^-$ are determined in each vial. In order to minimize variations in diffusivity for membranes attached to the various vials in a sampler, the ^{36}Cl[AOX] in each vial is normalized with respect to the $^{36}Cl^-$ remaining in that vial. Comparison of the AOX in a live vial to that in neighboring sterilized vials provides the amount of biodegraded AOX.

Biodegradation of size-fractionated samples

In our second approach, AOX and COD samples were taken at the inlet and outet of the secondary treatment system, analyzed whole, after coarse filtration (CF) to remove solids, and after refiltration (DF: double filtered) through a 500 Da membrane. The final permeate represents the lower molecular weight potentially biodegradable fraction. Comparison of the decrease in AOX and COD across the treatment system in the coarse and fine filtrates should be a measure of biodegradation. For example, if extensive biodegradation occurred, then the double-filtered AOX should decrease much faster than the whole or coarse-filtered compounds.

Description of the field site

Field work was done at the Georgia-Pacific mill at Brunswick GA. The mill pulps both hardwood and softwood in 19 digesters, 8 for hardwood and 11 for pine. Three bleach lines (ClO_2) are run; two process pine, and one swings between hardwood and pine. Total production is about 2150 tons/day. The sequence used is D-Eop-D-Ep-D. A primary clarifier with a holding capacity of 12.3 million gallons is operated at a rate of 20-24 million gallons/day. Secondary treatment occurs in a 12-acre presettling basin, a 137-acre aerated lagoon, and a 6-acre settling lagoon for a total retention of 6 days. Additional aerators were added and water usage was reduced while this study was in progress. The lagoon currently has 61 surface aerators, and total flow to the river is presently about 35 mgd. A schematic of the ASB is attached as Figure 1.

Experimental

Preparation of $^{36}ClO_2$

Labeled ClO_2 was prepared by the Bray method (13) from tagged potassium chlorate and oxalic acid according to the equation

$$2\ K^{36}ClO_3 + 2\ (COOH)_2 \Rightarrow 2^{36}ClO_2 + 2\ CO_2 + (COOK)_2 + 2\ H_2O \qquad (7)$$

In a typical experiment, $K^{36}ClO_3$ (9.4 g, 24 μCi) and oxalic acid (33 g) were mixed in a round bottom flask. The flask was connected to a trap containing 200 mL of ice water to collect the $^{36}ClO_2$. In order to prevent release of radioactive gas, the outflow from the trap was fed to two gas scrubbers containing 200 mL of 150 g/L and 100 g/L of KI respectively. The flask was placed in a 60°C constant temperature bath, swept continuously with nitrogen, and the reaction was initiated by adding 5 mL of water. The reaction was run for 3 hours; longer reaction did not materially increase yield, possibly because of ClO_2 loss from the trap. The ClO_2 yield was 1.4 g (3.1 μCi) in 200 mL. A side reaction generated $^{36}Cl_2$ at about 4% of the ClO_2 mass. To quench this Cl_2, $NaClO_2$ (2.6 g. per g. of Cl_2) crystals were added to the ClO_2 solution. The radioactive Cl_2 is converted to sodium chloride according to the equation

$$2\ NaClO_2 + {}^{36}Cl_2 \Rightarrow ClO_2 + 2\ Na^{36}Cl \qquad (8)$$

Hence ClO_2 is the only radioactive bleaching reagent produced. It was stored in the dark at 4°C; its concentration decreased by about 14% over three weeks.

Tagged potassium chlorate was prepared through the equilibrium

$$2\ ClO_2^- \Leftrightarrow ClO_3^- + Cl^- \qquad (9)$$

Addition of $^{36}Cl^-$ to a solution of sodium chlorate in HCl led to isotope incorporation into chlorate. $H^{36}Cl$ (300 μCi, sp. act. 13 mCi/g, from New England Nuclear) was added to a solution of 10 g $NaClO_3$ and 500 μL conc. HCl in 20 mL water. The solution was heated to 80°C for 4h. Solid KOH (5.5g) was then added, and the solution was chilled, upon which $K^{36}ClO_3$ crystallized out. The crystals were washed three times by adding 5 mL of water and stirring for 30 min. A total of 9.4 g. $KClO_3$ (24 μCi) was obtained.

Preparation of $^{36}Cl_2$

$^{36}Cl_2$ was prepared according to a published procedure (14). Briefly, 100 μCi of $H^{36}Cl$ was added to 200 mL of chlorine water (6.57 g/L) and stirred for a few hours. The isotope exchanges into Cl_2 through equilibria such as

$$Cl_2 + Cl^- \Leftrightarrow Cl_3^- \qquad (10)$$

and

$$Cl_2 + H_2O \Leftrightarrow HOCl + HCl \qquad (11)$$

Pulp Bleaching

Softwood brownstock pulp obtained from Georgia-Pacific's Brunswick mill was bleached with either Cl_2 (0.026 g. Cl_2/g. oven dried, or OD, pulp), or ClO_2 (0.058 g. Cl_2/g. OD pulp). A slurry of 2% OD pulp in water at 50°C was stirred for 1 hour with the bleach in a sealed 500 mL flask. The pulp was then washed and extracted with 2.4% NaOH at 60°C for 1 hour. The residual chlorine in the bleaching stage filtrate was <0.02 g/L Cl_2. In a typical run, the distribution of radioactivity corresponding to organic and inorganic chlorine in the pulp and filtrate was as follows. The activity in the bleach filtrate is associated with AOX as well as with chloride.

	ClO_2-bleaching	Cl_2-bleaching
bleaching-stage filtrate:	91.5%	70.6%
extraction-stage filtrate:	7.6%	11.6%
pulp:	2.5%	2.9%
unaccounted:	-1.6%	15%

Analysis of radioactive AOX

Since analysis of our radioactive samples with a conventional AOX analyzer would contaminate the instrument, an alternate procedure was developed. In the conventional Method 1650A method (15) of AOX determination, the sample is sorbed on granular charcoal, the inorganic chloride is displaced from the charcoal with a nitrate rinse, and the charcoal is combusted converting the AOX to HCl, which is then determined through argentometric titration. We eliminated the combustion step. Instead, we counted the original solution and the nitrate rinsate (which contained the chloride fraction), and determined the AOX by difference. The procedure used is as follows.

The sample (5 mL) is mixed with water (10 mL) and 2 mL of a nitrate solution containing 20 g. KNO_3 and 1.4 mL HNO_3 per liter. Two 2-mL aliquots are withdrawn and counted. This provides the total ^{36}Cl in the system from both AOX and chloride ion. Five scoops of granular activated charcoal are then added, the sample is shaken for two hours and then filtered through a 0.45 μm filter. The charcoal sorbs both organic and inorganic chlorine. Chloride ion is now removed from the charcoal by rinsing it with 2 mL of the nitrate solution. The filtrate and rinsate are counted, and the AOX sorbed on the charcoal is obtained by difference. Accuracy, determined from processing 9 $^{36}Cl^-$ samples was 103.1%; σ=1%.

Kinetics of diffusion of chloride and AOX from the vials

In order to verify that diffusion of chloride and AOX through the membranes followed first order kinetics, a concentrated bleach filtrate was placed in vials capped with membranes. The vials were immersed in a tank of water whose contents were changed twice daily to keep the concentration of substrate (Cl^- or AOX) to near-zero outside the vials. Two vials were removed daily and analyzed for $^{36}Cl^-$ and ^{36}Cl[AOX]. The results averaged from two studies were consistent with first-order kinetics ($r>0.95$). First-order behavior was also previously observed with benzene, toluene and xylene in a groundwater application (12).

Sorption to biomass

To determine the degree of AOX sorption to biomass, some of the field samples were analyzed for AOX associated with filterable solids. A 1 mL aliquot from field samples representing both high (80,000 mg/L) and low (80 mg/L) solids levels was filtered through a 0.45 μm polycarbonate track-etched filter obtained from Poretics. The filter was then rinsed with a 2 mL 0.25M nitrate solution, which was counted. Controls were run that the retention of $^{36}Cl^-$ on biomass was minimal. In all cases AOX adsorption to solids was between 1and 6%.

Transport of ions through the membrane

In order to verify that inorganic ions were able to move through the membrane, surface samples were taken at two different times from from vials placed in the treatment system on April 1994 at the location of aerator 21. The samples inside the vials were analyzed for chloride and chlorate by ion chromatography. The results shown below demonstrate that Cl^- equilibrates in less than a day, and that substantial chlorate ingress occurs in a day.

	chloride (ppm)	chlorate (ppm)
lagoon sample	527	1680
vial sample (24 hr.)	508	936
vial sample (96 hr.)	527	1411

Field Measurements

Two types of field measurements were made for dissolved oxygen (DO), BOD, suspended solids, COD, and total Kjeldahl Nitrogen (TKN). Data averaged over depth at each location are provided in Table 1. The DO is essentially nonexistent. The suspended solids tend to vary throughout the treatment system, but in general, the concentration decreases across the lagoon. The BOD falls across the lagoon; the COD declines much more slowly. Total Kjeldahl nitrogen showed that there was sufficient nutrient available.

AOX and COD measurements for the second approach involving the double and coarse filtered samples were made on 24 hour composites. Samples were collected and processed in three different ways: (i) as is, (ii) coarse-filtered (CF) through a 0.8 μ fiberglass filter, and (iii) filtered again through a 500 Da cut-off filter (DF: double-filtered). COD was determined at the mill; AOX was run at Triangle Laboratories at Research Triangle Park, NC.

Results and Discussion

In-situ biodegradation

Two probes were run in parallel at each location, one for Cl_2-bleached, and the other for ClO_2-bleached AOX. Results from a typical run for the Cl_2 probe are illustrated in Table 2. The live and sterile cells were typically alternated in each probe. Some probes contained a group of closely placed live cells at effectively the same depth to determine precision. For example, there are five live vials placed at 11 feet for the probe for Cl_2-bleached AOX. The third and fourth columns provide the activity of AOX and Cl^- recovered (dpm), respectively,

third and fourth columns provide the activity of AOX and Cl^- recovered (dpm), respectively, from the vials at the end of the experiment. These are averaged from two measurements. The eighth column provides the amount of AOX expected to be lost through diffusion alone as described earlier; for a given sample, the results are averaged from calculations made with the sterile vial immediately above and below the live vial under consideration. The difference between the AOX recovered and the AOX expected to be lost through diffusion is then assigned to biodegradation.

If diffusion from the vials was uniform, then the percent chloride recovered should be the same for each sample. The variability observed could arise from differences in flow patterns, partial blockage of the membranes, inhomogeneity in membrane construction, etc. However, these variations should influence AOX loss in the same manner as they affect Cl^- diffusion, in which case, normalizing the AOX loss with reference to chloride diffusion should minimize the variability. As a practical matter, normalizing does not make a major difference to the results, confirming the absence of appreciable differences in diffusivity. However, in some cases, where the bottom sample was buried in the sludge bed or where the top sample was exposed due to fluctuations in the water level, the residual AOX was high. These were easily flagged as outliers, since the Cl^- was also correspondingly high.

The September 1994 results from a non-aerated zone at Brunswick shown in Figure 2 indicate that we have biodegradation for both Cl_2- and ClO_2-derived AOX. It also suggests a weak depth dependence, which, however, could not be confirmed elsewhere. That any depth dependence is weak is not surprising, since there is vertical mixing even in the non-aerated region of the lagoon. Comparison of the Figure 2 results with those in Figure 3, which come from probes placed close to a surface aerator, show that the degradation rates average between 6 and 14%.

Results from a field trip undertaken in January 1995 were consistent with those from September 1994. The AOX removal profiles at aerator 3 and aerator 34 at Brunswick are illustrated in Figures 4 and 5, respectively. These are the last and first aerators in the treatment system. Clearly, AOX biodegradation at various locations at different times is only about 10-20%. The biodegradation at each location averaged across depth is summarized in Table 3.

These results contain several apparent anomalies. First, Brunswick reports a 50% total removal for AOX. Yet, our values (which only represent the biodegradation component) are much lower suggesting that mechanisms other than water column biodegradation are responsible for the bulk of AOX removal. A small part of the AOX will strip into the atmosphere, but volatile AOX only constitutes a small fraction of the total AOX. Chemical degradation is another possibility, but this is unlikely to be the exclusive mechanism since an AOX sample taken from the inlet does not degrade appreciably when stored over a week. The most likely mechanism is deposition in the pre-settling zone, possibly after association to the mostly fibrous solids present.

While sorption is implicated as a possible route for AOX removal, it should be recognized that the propensity for AOX to sorb to biomass is actually quite low. Sorption to biomass is favored for hydrophobic compounds, and the octanol:water partition coefficient is typically used as an index of hydrophobicity. Generally, a compound is considered to have appreciable sorption potential if the partition coefficient exceeds 1000. For AOX, this value is less than one (14) suggesting a low potential for sorption. Yan and Allen (16) have confirmed this, as we have also in the present study. Hence, for sorption to be important for AOX, there needs to be high levels of solids present in the system. However, this is the case in the pre-settling zone, which could account for some of the drop in AOX across this region. These conclusions also apply to the non-biodegradable component of COD. As with AOX, the data in Table 1 suggest that most (but not all) of the COD reduction also occurs early in the treatment system. We (17) and others (7,18-20) have shown that concentrations of AOX and non-biodegradable COD are related at the outfall, which suggests that the same removal mechanism applies to both species.

The average biodegradation at Brunswick is identical for both ClO_2- and Cl_2-derived AOX at 15%. Bryant et al. (21) and Barton and Drake (22) have both concluded that differences in the degree of ClO_2 substitution does not significantly change lagoon efficiency. A point of difference between their studies and ours is that their work applies to all the removal pathways, and not just to biodegradation.

Biodegradation of size-fractionated samples

The COD profiles are provided in Figure 6. The black bars are for the whole samples; the hatched bars represent the CF material; and the clear bars stand for the DF samples. The DF samples represent the potentially biodegradable fraction, since compounds larger than 500 Da cannot easily penetrate a microorganism. As expected, the variability decreases from the inlet to the outfall because of mixing in the lagoon. Approximately 20% of the inlet COD is particulate (unfiltered minus CF); this drops to 6% at the outfall, presumably because of settling. The CF and DF COD average to 1200 ppm and 570 ppm, respectively. The difference, 630 ppm, represents non-biodegradable COD. This value compares well to the average outfall CF COD of 600 ppm. Hence, approximately 43% of the inlet dissolved COD is biodegradable; the remainder traverses the treatment system relatively unhindered. The degree of biodegradation is illustrated by the inlet and outlet comparison of the DF:CF COD ratios in Figure 7.

The AOX profiles illustrated in Figure 8 are very different from those for COD. Only 11% of the inlet AOX is of high molecular weight (>500 Da). The ratio of DF:CF AOX decreases to a much smaller extent across the lagoon as shown in Figure 9, demonstrating that the DF fraction decreases only slightly faster than the CF. The decrease would have been much sharper for the DF material if biodegradation was a major removal mechanism. The small decrease in the inlet:outfall AOX ratio in Figure 9 translates to about 15% biodegrada-

Samples for AOX analysis were collected on two occasions at two additional sites (aerators 23 and 28) located at the front end of the treatment system. The results are compared to inlet and outfall AOX in Table 4. Clearly, most of the decrease takes place before the AOX reaches the two aerators, which indicates that most of the reduction occurs in the pre-settling zone and/or early in the lagoon. The decrease in CF AOX from these two locations to the outfall is 13%, only slightly lower than the 15% value inferred earlier. Thus, three independent lines of evidence: our radioactive work, the DF:CF AOX ratios, and the decrease in AOX from locations early in the lagoon to the outfall all support an approximately 15% AOX biodegradation in the water column of the Brunswick ASB.

Comparison of inlet and early-lagoon AOX reveals a decrease of more than 40%. Only a small fraction of this can be attributed to biodegradation, since the DF:CF ratio is relatively constant. Volatilization probably accounts for a small fraction of the loss (6,23) , but most of the organochlorine generated is relatively involatile. The two possible remaining mechanisms are chemical degradation and settling, and evidence to distinguish between the two is presently unavailable. It is interesting that while the whole:CF COD decreases from 1.28 at the inlet to 1.06 at the outfall as particulates settle out, the opposite is true for AOX where the whole:CF ratio increases slightly from 1.06 to 1.11. Larrea et al. (24) have observed that 18% of Kraft lignin condenses to particulate material during aeration. If condensation also occurred for AOX, then the increase in the ratio could be explained.

Finally, our results are to be compared with the results of Aprahamian and Stevens (18) who compared influent and effluent AOX and TOC in a 70% ClO_2 substituted mill both before and after filtration through a 1000 Da membrane. Their TOC reductions of 76% (whole) and 45% (filtered) across the lagoon compares well to our corresponding COD values of 79% and 48%, respectively. Their decrease in AOX (63% filtered, 40% whole) is also similar to that observed by us.

Summary

We have developed a new technique for measuring in-situ biodegradation at specific locations in secondary treatment systems. The method offers partially controlled conditions in a field setting, and should be useful in situations where a complex field environment cannot be readily reproduced in a laboratory. When applied to bleached pulp mill effluent, the method demonstrates that only 15% of the AOX biodegrades, and that AOX and COD removal occurs very early in the treatment system. Hence, adding greater aeration capacity to improve BOD reduction should have no effect on AOX removal, as observed at Brunswick. The 15% value was confirmed independently by measuring inlet and outfall AOX and COD for whole samples and for sub-samples size-fractionated to < 500Da. While the COD subsamples degraded much more rapidly than the whole sample, the fractionated AOX was removed only 15% faster than the whole AOX. Thus, biodegradation is the principal removal mechanism for COD, but not for AOX.

Acknowledgment

This study was funded by the the Georgia Consortium for Technological Competitiveness in Pulp and Paper, the Georgia-Pacific Corporation, and the member companies of the Institute of Paper Science and Technology. Portions of the work will be used by CW as partial fulfillment for the Ph.D. degree at the Institute.

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Table 1. Field parameters at Brunswick								
location	date	DO mg/L	temp (°C)	susp. solids (% VSS) mg/L	BOD mg/L	COD mg/L	BOD/ COD	TKN mg/L
end of pre-settling basin	12-28-94	0.2	29	170 (35)	102	984	0.10	
aer. 34	12-29-94	0.2	30	119 (31)	145	1026	0.14	
aer. 36	12-1-93	0.2	27	116	126			
	9-9-94	0.1	35	117	85	776	0.11	2.2
MP	9-9-94	0.1	34	80	75	731	0.10	3.2
aer. 13	12-1-93	0.6	24	87	68			
aer. 11	4-25-94	0.1	31	131 (48)	47			10.6
aer. 21	4-25-94	0.1	30	139 (59)	33			2.3
	9-8-94	0.15	31	82	56	684	0.082	3.7
aer. 3	12-30-94	0.2	22	77 (27)	40	797	0.037	
near end of lagoon	12-28-94	0.8	20	74 (29)	26	787	0.033	

Table 2: AOX biodegradation for aerator 3 at Brunswick (4.94)								
depth (ft)	condition	AOX recovered (dpm)	Cl^- recovered (dpm)	AOX recovered (%)	Cl^- recovered (%)	k_{AOX}/k_{inorg}	AOX diffusion (%)	AOX biodeg (%)
20	sterile	33,200	23,810	90.3	3.9	0.03	80.2	
19	live	29,800	45,170	81.1	7.4	0.08	87.9	7.73
18	sterile	28,810	16,980	78.4	2.8	0.07	84.3	
17	live	27,350	42,760	74.4	7.0	0.11	83.9	11.3
16	sterile	29,130	16,390	79.3	2.7	0.06	81.1	
15	live	28,280	40,860	76.9	6.7	0.10	85.9	10.43
14	sterile	31,140	19,520	84.7	3.2	0.05	79.4	
13	live	28,520	45,820	77.6	7.5	0.10	85.9	9.65
12	sterile	28,800	18,220	78.3	3.0	0.07	79.2	
11	live	26,100	49,500	71.0	8.1	0.14	82.4	13.8
11	live	25,470	38,480	69.3	6.3	0.13	80.8	14.2
11	live	26,370	34,900	71.7	5.7	0.12	80.2	10.5
11	live	25,150	35,450	68.4	5.8	0.13	80.3	14.8
11	live	26,880	44,000	73.1	7.2	0.12	81.6	10.4
10	sterile	26,840	15,110	73.0	2.5	0.08	75.6	
9	live	25,760	36,910	70.1	6.0	0.13	79.1	11.4
8	sterile	27,280	15,970	74.2	2.6	0.08	74.6	
7	live	32,550	45,930	88.6	7.5	0.05	81.5	-8.62
7	live	32,680	45,910	88.9	7.5	0.05	81.5	-9.04
6	sterile	28,310	19,620	77.0	3.2	0.08	76.7	
5	live	24,760	37,200	67.4	6.1	0.14	81.2	17.1
4	sterile	27,940	14,140	76.0	2.3	0.07	74.0	
3	live	24,020	32,390	65.4	5.3	0.14	79.4	17.7
2	sterile	26,350	11,620	71.7	1.9	0.08	74.9	
1	live	24,180	27,400	65.8	4.5	0.13	77.0	14.6

Table 3: AOX biodegradation at various Brunswick locations			
location	bleach	Percent biodegradation (σ)	n
non-aerated	Cl_2	12 (4)	8
	ClO_2	12 (6)	11
aerator 34	ClO_2	14 (6)	8
	Cl_2	6 (8)[1]	10
aerator 3	Cl_2	18 (14)	12
	ClO_2	10 (8)	15
aerator 36	Cl_2	24 (17)	7
	ClO_2	24 (11)	6
[1]an outlier was dropped before averaging			

Table 4: AOX (ppm) at various locations in the treatment system				
	whole	CF	DF	DF/CF
inlet	9.33	8.85	7.85	0.89
aerator 23	5.36	5.09	3.99	0.77
aerator 28	5.53	4.98	3.77	0.76
outfall	4.74	4.27	3.41	0.80

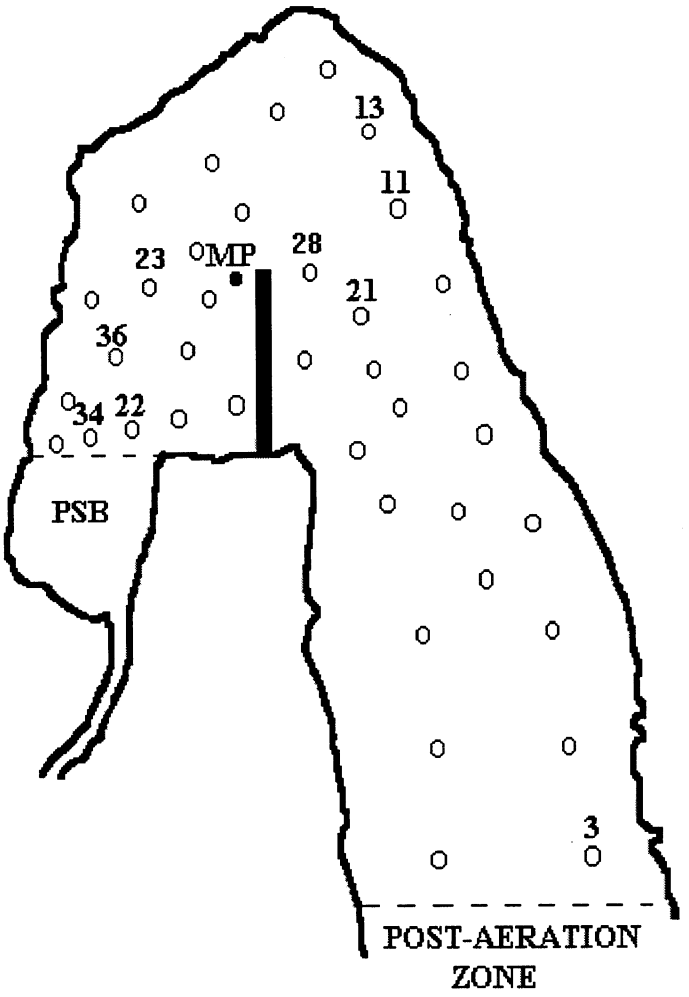

Figure 1: The secondary treatment system at the Georgia-Pacific Brunswick mill. PSB refers to the pre-settling basin.

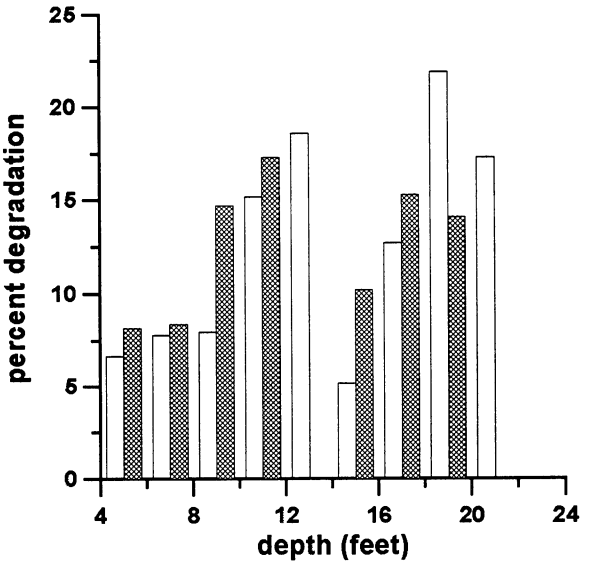

Figure 2. Biodegradation of Cl_2-derived (cross-hatched) and ClO_2-derived (unshaded) AOX in a non-aerated zone

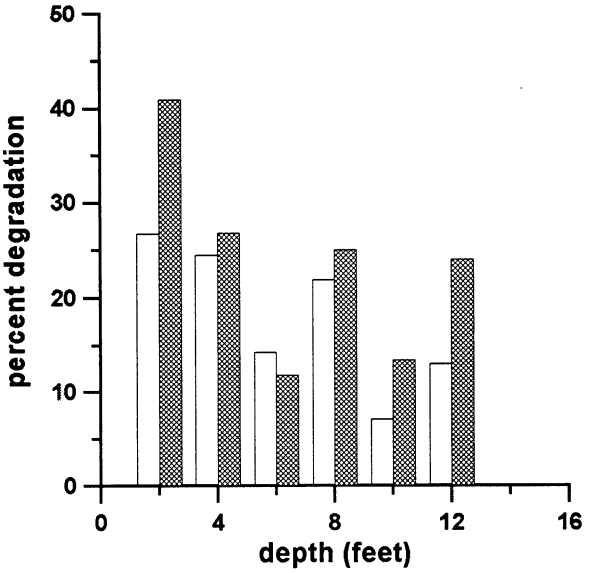

Figure 3. Biodegradation of Cl_2-derived (cross-hatched) and ClO_2-derived (unshaded) AOX at aerator 36

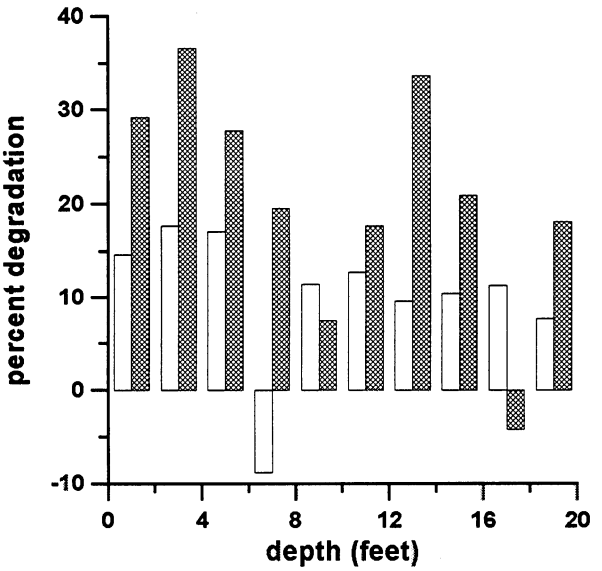

Figure 4. Biodegradation of Cl_2-derived (cross-hatched) and ClO_2-derived (unshaded) AOX at aerator 3

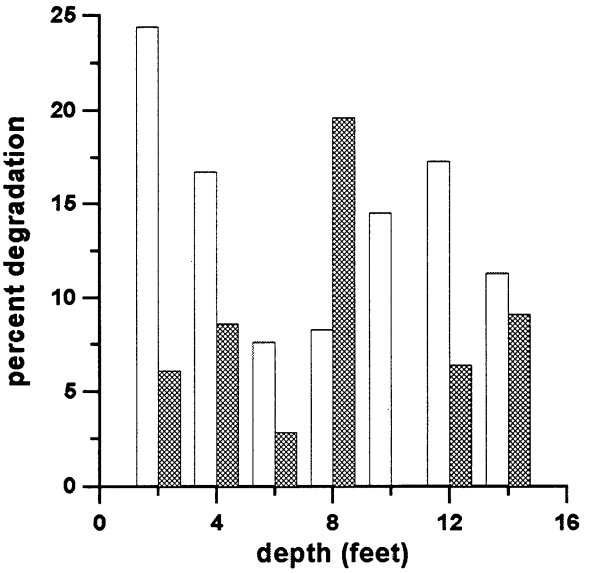

Figure 5. Biodegradation of Cl_2-derived (cross-hatched) and ClO_2-derived (unshaded) AOX at aerator 34

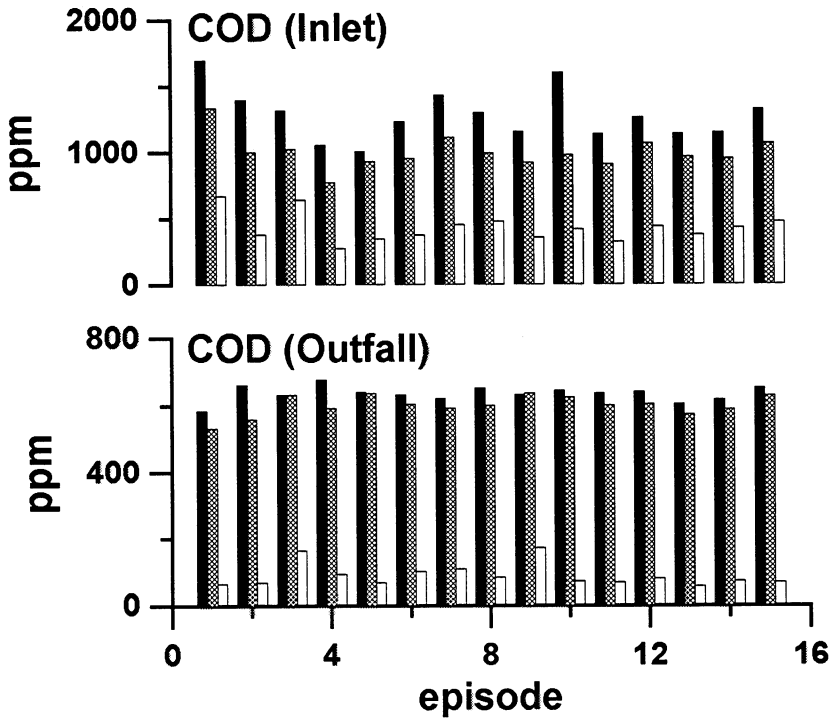

Figure 6: Whole (black), coarse-filtered (hatched), and double-filtered (unshaded) COD

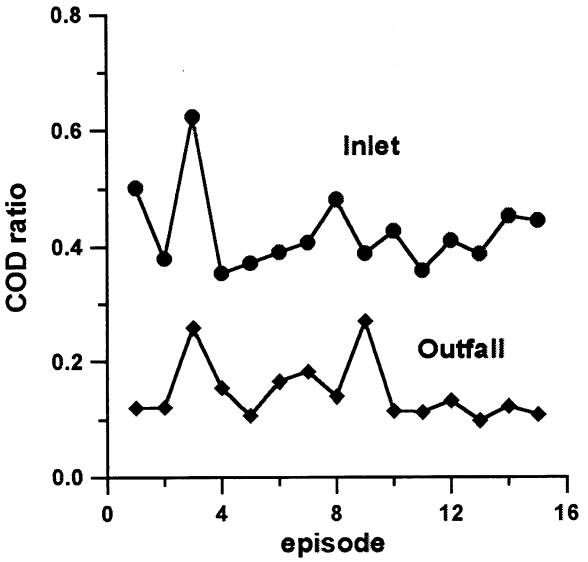

Figure 7: Ratio of DF:CF COD

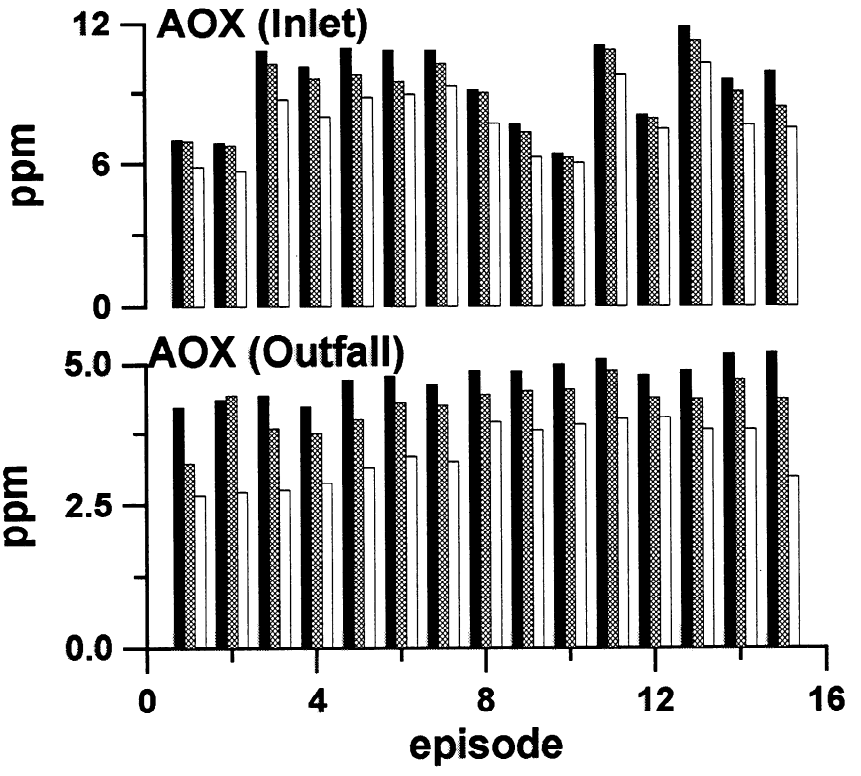

Figure 8: Whole (black), coarse-filtered (hatched), and double-filtered (unshaded) AOX

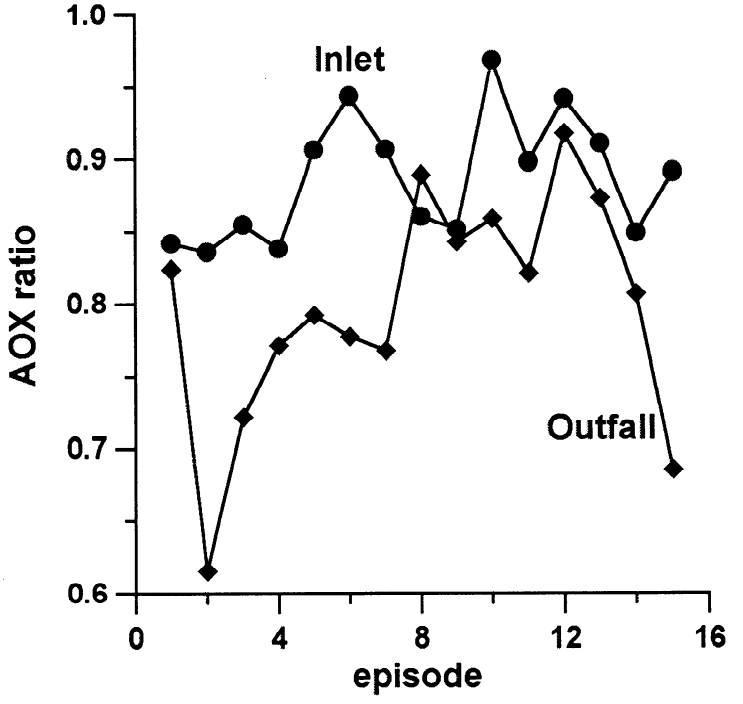

Figure 9: Ratio of DF:CF AOX